United States
Environmental Protection
Agency

Office of Air Quality
Planning And Standards
Research Triangle Park, NC 27711

EPA-454/R-96-008
November 1996

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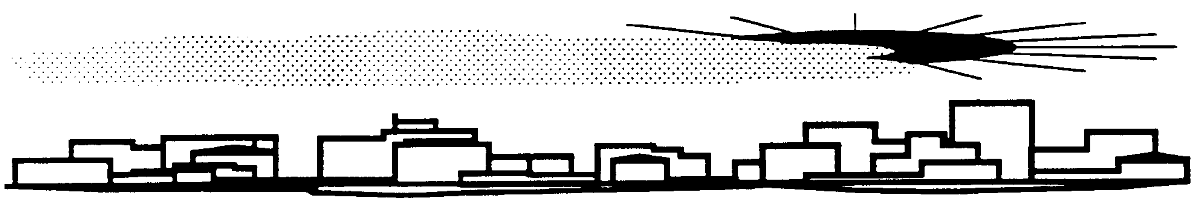
EPA

LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF 1,3-BUTADIENE



L & E

EPA 454/R-96-008

LOCATING AND ESTIMATING AIR EMISSIONS FROM SOURCES OF 1,3-BUTADIENE

Office of Air Quality Planning and Standards
Office of Air and Radiation
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EXECUTIVE SUMMARY

The 1990 Clean Air Act Amendments contain a list of 189 hazardous air pollutants (HAPs) which the U.S. Environmental Protection Agency must study, identify sources of, and determine if regulations are warranted. One of these HAPs, 1,3-butadiene (butadiene), is the subject of this document. This document describes the properties of butadiene as an air pollutant, defines its production and use patterns, identifies source categories of air emissions, and provides butadiene emissions data in terms of emission factors and national inventory estimates. The document is a part of an ongoing EPA series designed to assist the general public at large, but primarily State/local air agencies, in identifying sources of HAPs and determining emissions estimates.

Butadiene is primarily used in the manufacture of synthetic elastomers (rubbers, latexes) and for producing raw materials for nylon. Butadiene is emitted into the atmosphere from its production, its use as a chemical feedstock in the production of other chemicals, the use of these other chemicals, mobile sources, and from a wide variety of miscellaneous processes involving fossil fuel and biomass combustion, petroleum refining, secondary lead smelting, and wastewater treatment.

Including only sources for which estimates are available or can be calculated, total nationwide emissions are estimated at 121,002 tons per year (109,775 Mg/yr). The primary sources of butadiene emissions on a national level are on-road mobile (47%) and off-road mobile (35%). Table ES-1 illustrates the national emissions estimates developed for the more predominant butadiene categories. The main butadiene air emissions sources are on-road mobile, off-road mobile, biomass burning, butadiene users, and petroleum refining. Some of these estimates for the non-fuel combustion sources were obtained from the reports required under the Superfund Amendment and Reauthorization Act (SARA), Title III, Section 313. Other estimates are a function of national activity data combined with the best available emission factors.

Table ES-1. National Emission Estimates by Source Category[a]

	Source	Applicable Year	Tons (Mg)	Percent
Mobile	On-road	1992	56,786 (51,517)	47.3
	Off-road	1990	41,883 (37,996)	34.9
	General aviation and air taxis	1994	107 (97)	0.1
Stationary	Biomass burning (forest fires & prescribed burning)	1989	19,931 (18,082)	16.0
	Major butadiene users[b]	1992	1,405 (1,275)	1.2
	Petroleum refining	1992	219 (199)	0.2
	Butadiene production	1992	191 (173)	0.2
	Secondary lead smelting	1990	134 (122)	0.1
	Miscellaneous other sources[c]	1992	106 (96)	0.1
Total			121,049 (109,004)	100.1

[a] Only sources for which estimates were available or could be calculated are included. For example, emissions from open burning of tires have not been included.

[b] Includes following SIC Codes:

28	Chemicals and allied products
2812	Alkalies and chlorine
2819	Industrial inorganic chemicals, nec
2821	Plastics materials synthetic resins and nonvulcanizable elastomers
2822	Synthetic rubber (vulcanizable elastomers)
2865	Cyclic organic crudes and intermediates, and organic dyes and pigments
2869	Industrial organic chemicals, nec
2879	Pesticides and agricultural chemicals, nec
2891	Adhesives and sealants
2899	Chemicals and chemical preparations, nec

[c] Other sources reporting under SARA 313 include facilities identified with the following SIC Codes. Also included are two facilities without SIC Codes but which account for 15 tons per year (14 Mg/yr) combined, and one facility with an SIC Code that is not listed but which reported 0.04 tons per year (0.04 Mg/yr).

2046	Wet corn milling
2369	Girl's, children's, and infant's outwear, nec
2621	Paper mills
3312	Steel works, blast furnaces (including coke ovens), and rolling mills
3579	Office machines, nec
8731	Commercial physical and biological research

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SECTION 1.0

PURPOSE OF DOCUMENT

The U.S. Environmental Protection Agency (EPA), State, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, limited information is available on the ambient air concentrations of these substances or about the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of locating and estimating (L&E) documents such as this one that compiles available information on sources and emissions of these substances. Other documents in the series are listed below:

Substance	EPA Publication Number
Acrylonitrile	EPA-450/4-84-007a
Benzene (under revision)	EPA-450/4-84-007q
Cadmium	EPA-454/R-93-040
Carbon Tetrachloride	EPA-450/4-84-007b
Chlorobenzene (update)	EPA-454/R-93-044
Chloroform	EPA-450/4-84-007c
Chromium (supplement)	EPA-450/2-89-002
Chromium	EPA-450/4-84-007g
Coal and Oil Combustion Sources	EPA-450/2-89-001

Substance	EPA Publication Number
Cyanide Compounds	EPA-454/R-93-041
Epichlorohydrin	EPA-450/4-84-007j
Ethylene Dichloride	EPA-450/4-84-007d
Ethylene Oxide	EPA-450/4-84-007l
Formaldehyde	EPA-450/4-91-012
Manganese	EPA-450/4-84-007h
Medical Waste Incinerators	EPA-454/R-93-053
Mercury and Mercury Compounds	EPA-453/R-93-023
Methyl Chloroform	EPA-454/R-93-045
Methyl Ethyl Ketone	EPA-454/R-93-046
Methylene Chloride	EPA-454/R-93-006
Municipal Waste Combustors	EPA-450/2-89-006
Nickel	EPA-450/4-84-007f
Perchloroethylene and Trichloroethylene	EPA-450/2-89-013
Phosgene	EPA-450/4-84-007i
Polychlorinated Biphenyls (PCBs)	EPA-450/4-84-007n
Polycyclic Organic Matter (POM) (under revision)	EPA-450/4-84-007p
Sewage Sludge Incinerators	EPA-450/2-90-009
Styrene	EPA-454/R-93-011
Toluene	EPA-454/R-93-047
Vinylidene Chloride	EPA-450/4-84-007k
Xylenes	EPA-454/R-93-048

In addition, new documents currently under development will address lead, chlorinated dibenzo-p-dioxins and chlorinated dibenzofurans, and arsenic and arsenic compounds.

This document deals specifically with 1,3-butadiene, commonly referred to as butadiene. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of 1,3-butadiene and estimating their air emissions.

Because of the limited availability of data on potential sources of 1,3-butadiene emissions and the variability in process configurations, control equipment, and operating procedure among facilities, this document is best used as a primer on (1) types of sources that may emit 1,3-butadiene, (2) process variations and release points that may be expected, and (3) available emissions information on the potential for 1,3-butadiene releases into the air. The reader is cautioned against using the emissions information in this document to develop an exact assessment of emissions from any particular facility. For facilities, most estimates are values reported by the facilities in 1984 in response to EPA requests for information and therefore may be out of date. Furthermore, not all facilities received requests, and those that received requests did not always provide complete responses. For more accurate estimates, the reader should seek more current and complete data.

It was thought at one point that the 1984 Chemical Manufacturers Association (CMA) facility data could be updated using the Toxic Release Inventory (TRI). However, because many of the chemical production facilities produce multiple chemicals, it was not possible to accurately apportion the TRI data to the specific CMA facilities.

An effort was made to obtain more up-to-date information than the 1984 data. A literature search was conducted and several databases were accessed. The most promising sources of potential data are the current Polymers/Resins National Emission Standard for Hazardous Air Pollutants (NESHAP) and Rubber Chemicals work. The polymers/resins NESHAP was to have been completed and published by fall, 1994, but because of the confidentiality of much of the data, it was not possible to obtain those data at the present time to include in this L&E document. The process descriptions in this L&E document should not differ greatly from those in the NESHAP. However, it is not certain at this time what data will be available from the NESHAP and how the data might differ from what is presently in the L&E.

The rubber chemicals work has been delayed, so that EPA can expand the definition of "rubber chemicals" to include a broader category of chemicals. It is not expected that information will be available in time to be included in this version of the Butadiene L&E.

It is possible, in some cases, that orders-of-magnitude differences may result between actual and estimated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in all situations where an accurate assessment of 1,3-butadiene emissions is necessary, the source-specific information should be obtained to confirm the existence of particular emitting operations and the types and effectiveness of control measures, and to determine the impact of operating practices. A source test and/or material balance calculations should be considered as the best method of determining air emissions from an operation.

Most of the emission factors for the basic production and intermediate product sources presented in the text are based on the 1984 data. The supporting facility-specific data are provided in Appendix C. The emission rates for equipment leaks were developed by the CMA and are based on a 1989 study of equipment leak emissions at butadiene production facilities. These CMA rates are significantly different from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) average emission rates,[1] and, because they are specific to butadiene, are assumed to better represent equipment leak emissions at other butadiene user facilities; therefore, they were used to estimate annual emissions. Again, the reader should collect facility-specific data for the most accurate estimates.

The chemical industry as a whole has done a lot to reduce emissions since the early/mid 1980s as interest in air toxics has grown. A number of National Emission Standards for Hazardous Air Pollutants (NESHAP) have been promulgated that are expected to reduce butadiene emissions from facilities that are subject to the regulatory requirements. The recent NESHAP that will impact butadiene emissions the most include the Hazardous Organic NESHAP (HON) which has been promulgated April 22, 1994 and NESHAP for several of the Polymers and Resins categories that are under development. Others include the NESHAP for Publicly Owned Treatment Works, the Petroleum Refineries NESHAP and the NESHAP for secondary lead production. Specific requirements and impacts are not included in this document. The reader should refer to the regulations to assess the reductions achieved.

The EPA also initiated a voluntary program in 1991 as a part of the Agency's pollution prevention strategy. Known as the 33/50 Program, companies committed to reducing facilities emissions for 17 high priority compounds. Although butadiene is not among the listed compounds, reductions would be achieved where butadiene was co-located with a listed compound or where shared equipment was modified to reduce emissions of the 17 high priority compounds.

In addition to the information presented in this document, another potential source of emissions data for 1,3-butadiene from facilities is the Toxic Chemical Release Inventory (TRI) form required by Title III, Section 313 of the 1986 Superfund Amendments and Reauthorization Act (SARA).[2] Section 313 requires owners and operators of facilities in certain Standard Industrial Classification Codes that manufacture, import, process, or otherwise use toxic chemicals (as listed in Section 313) to report annually their releases of these chemicals to all environmental media. As part of SARA 313, EPA provides public access to the annual emissions data.

The TRI data include general facility information, chemical information, and emissions data. Air emissions data are reported as total facility release estimates for fugitive emissions and point source emissions. No individual process or stack data are provided to EPA under the program. SARA Section 313 requires sources to use available stack monitoring data for reporting but does not require facilities to perform stack monitoring or other types of emissions measurement. If monitoring data are unavailable, emissions are to be quantified based on best estimates of releases to the environment.

The reader is cautioned that TRI will not likely provide facility, emissions, and chemical release data sufficient for conducting detailed exposure modeling and risk assessment.

In many cases, the TRI data are based on annual estimates of emissions (i.e., on emission factors, material balance calculations, and engineering judgment). We recommend the use of TRI data in conjunction with the information provided in this document to locate potential emitters of butadiene and to make preliminary estimates of air emissions from these facilities.

For mobile sources, more data are becoming available for on-road vehicles. Additionally, the EPA model that generates emission factors undergoes regular update. The on-road mobile sources section in this document should therefore be viewed as an example of how emissions can be determined and the reader should look for more detailed data for the most accurate estimates.

Limited data on off-road vehicles and other stationary sources are available. However, with EPA's increased emphasis on air toxics, more butadiene data are likely to be generated in the future.

As standard procedure, L&E documents are sent to government, industry, and environmental groups wherever EPA is aware of expertise. These groups are given the opportunity to review a document, comment, and provide additional data where applicable. Where necessary, the document is then revised to incorporate these comments. Although this document has undergone extensive review, there may still be shortcomings. Comments subsequent to publication are welcome and will be addressed based on available time and resources. In addition, any information on process descriptions, operating parameters, control measures, and emissions information that would enable EPA to improve on the contents of this document is welcome. Comments and information may be sent to the following address:

Leader, Emission Factor and Methodologies Team
Emission Factor and Inventory Group (MD-14)
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

SECTION 2.0
OVERVIEW OF DOCUMENT CONTENTS

This section briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3.0 provides a brief summary of the physical and chemical characteristics of butadiene and an overview of its production, uses, and emissions sources. This background section may be useful to someone who needs to develop a general perspective on the nature of butadiene, how it is manufactured and consumed, and potential production, use, and mobile sources of emissions.

Section 4.0 focuses on the production of butadiene and the associated air emissions. For each major production source category described in Section 4.0, an example process description and a flow diagram with potential emission points are given. Available emissions estimates were used to calculate emission factor ranges that show the potential for butadiene emissions before and after controls employed by industry. Also provided are estimates of annual emissions from equipment leaks. Individual companies that are reported in trade publications to produce butadiene are named.

Section 5.0 describes major source categories that use butadiene, primarily in the manufacture of synthetic elastomers. For each major production process, a description(s) of the process is given along with a process flow diagram(s). Potential emission points are identified on the diagrams and emission ranges are presented as estimates are available. Ranges of annual emissions due to equipment leaks are also given. Individual companies that use butadiene as a feedstock are reported.

Section 6.0 provides a brief summary on butadiene emissions from mobile sources. The section addresses both on-road and off-road sources.

Section 7.0 summarizes the source categories--termed miscellaneous sources--that use and potentially emit smaller quantities of butadiene. It also addresses emissions from indirect sources such as treatment of butadiene-containing wastewater and other potential sources that are not clearly users or indirect sources ("other" category). Limited information on these sources is available; therefore, varying levels of detail on the processes, emissions, and controls are presented. Locations of facilities for each source category as identified in the literature are provided.

The final section, Section 8.0, summarizes available procedures for source sampling and analysis of butadiene. This section provides an overview of applicable sampling procedures and cites references for those interested in conducting source tests.

Appendix A presents a summary table of the emission factors contained in this document. This table also presents the factor quality rating and the Source Classification Code (SCC) or Area/Mobile Source (AMS) code associated with each emission factor.

Appendix B provides a brief description of the basis for the national emission estimates appearing in Section 3.0. For each source, there is a description of the estimation approach and an example calculation.

Appendix C provides facility-specific data taken from Section 114 responses upon which the process vent and secondary source emission factors in Sections 4.0, 5.0, and 7.0 are based. Each facility has been assigned a letter code to prevent disclosure of its identity. In general, the equipment leak emissions shown were calculated by applying average CMA emission factors to the equipment component counts from the Section 114 responses. The exceptions are butadiene producers and miscellaneous users. For producers, equipment counts were summarized by CMA for 9 of the 11 facilities and the resulting emissions are presented as the most recent data. For the miscellaneous users, estimates based on SOCMI factors were shown because equipment count data were not readily available to use with the average CMA emission factors. These were calculated in earlier work done by EPA.

Appendix D presents the procedure for the derivation of butadiene equipment leak emissions estimates associated with the production processes presented in Sections 4.0, 5.0, and 7.0. Calculations for pump seals and pressure relief valves appear as examples of these derivations.

Each emission factor listed in Sections 4.0 through 7.0 was assigned an emission factor rating (A, B, C, D, E, or U) based on the criteria for assigning data quality ratings and emission factor ratings as required in the document *Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections*.[3] The criteria for assigning the data quality ratings to source tests are as follows:

A - Test(s) was performed by a sound methodology and reported in enough detail for adequate validation. These tests are not necessarily EPA reference test methods, although such reference methods are certainly to be used as a guide.

B - Test(s) was performed by a generally sound methodology but lacked enough detail for adequate validation.

C - Test(s) was based on a nonvalidated or draft methodology or lacked a significant amount of background data.

D - Test(s) was based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

Once the data quality ratings for the source tests had been assigned, these ratings along with the number of source tests available for a given emission point were evaluated. Because of the almost impossible task of assigning a meaningful confidence limit to industry-specific variables (e.g., sample size vs. sample population, industry and facility variability, method of measurement), the use of a statistical confidence interval for establishing a representative emission factor for each source category was not practical. Therefore, some subjective quality rating was necessary. The following factor quality ratings were used in the emission factor tables in this document:

> <u>A - Excellent</u>. The emission factor was developed only from A-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough to minimize variability within the source category population.
>
> <u>B - Above average</u>. The emission factor was developed only from A-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category is specific enough to minimize variability within the source category population.
>
> <u>C - Average</u>. The emission factor was developed only from A- and B-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category is specific enough to minimize variability within the source category population.
>
> <u>D - Below average</u>. The emission factor was developed only from A- and B-rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population.
>
> <u>E - Poor</u>. The emission factor was developed from C- and D-rated test data, and there may be reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population.
>
> <u>U - Unrated or Unratable</u>. The emission factor was developed from suspect data with no supporting documentation to accurately apply an A through E rating. A "U" rating may be applied in the following circumstances:[4]

U1	=	Mass Balance (for example, estimating air emissions based on raw material input, product recovery efficiency, and percent control).
U2	=	Source test deficiencies (such as inadequate quality assurance/quality control, questionable source test methods, only one source test).
U3	=	Technology transfer.
U4	=	Engineering judgement.
U5	=	Lack of supporting documentation.

This document does not contain any discussion of health or other environmental effects of butadiene, nor does it include any discussion of ambient air levels.

SECTION 3.0
BACKGROUND

3.1 NATURE OF THE POLLUTANT

Butadiene is a colorless, flammable gas with a pungent, aromatic odor. It has a boiling point between 24.8 and 23°F (-4 and -5°C). Table 3-1 summarizes butadiene's chemical and physical properties.[5,6] Although butadiene is insoluble in water, it is slightly soluble in methanol and ethanol, and readily soluble at room temperature in common organic solvents such as benzene and ether.[7] It forms azeotropes with ammonia, methylamine, acetaldehyde, n-butene, and 2-butene.[5]

Butadiene is a highly versatile raw material that is used commercially in a variety of reactions. These include:

- Diels-Alder reactions with dienophiles to form a six-membered ring compound with a 2,3 double bond,
- conversion to cyclic or open chain dimers and trimers,
- telomerization with active hydrogen compounds,
- addition reactions with electrophilic and free radical compounds,
- oxidation reactions,
- substitution reactions, and
- polymerization.

TABLE 3-1. PHYSICAL AND CHEMICAL PROPERTIES OF 1,3-BUTADIENE

Property	Value
Structural Formula: C_4H_6, CH_2:CHCH:CH_2	
Synonyms: biethylene, bivinyl, butadiene, butadiene monomer divinyl, erythrene, methylallene, pyrrolylene, vinyl ethylene	
CAS Registry Number: 106-99-0	
Molecular Weight	54.09
Melting Point, °C	-108.91
Boiling Point, °C	-4.41
Partition Coefficient (log P, octanol/water)	1.99
Density at 20°C, g/cm^3	0.6211
Vapor Density	1.87
Critical Density, g/cm^3	0.245
Critical Temperature, °C	152
Critical Pressure, MPa (psi)	4.32 (626)
Critical Volume, mL/mol	221
Vapor Pressure, atm:	
15.3°C	2.0
47.0°C	5.0
Flash Point, °C	-105
Heat of Vaporization, J/g (cal/g):	
25°C	389 (93)
bp	418 (100)
Heat of Fusion, J/g (cal/g)	147.6 (35.28)
Heat of Formation at 25°C, kJ/mol (kcal/mol):	
Gas	110.2 (26.33)
Liquid	88.7 (21.21)
Free Energy of Formation at 25°C, kJ/mol (kcal/mol):	
Gas	150.7 (36.01)
Explosive Limits, vol % butadiene in air:	
Lower	2.0
Upper	11.5
Solubility in Water at 20°C, mg/L	735

Source: References 5 and 6.

Polymerization, with additions occurring at both the 1,2 and the 1,4 positions, are the basis for synthetic elastomer production, the major use of butadiene.[8]

Because of its reactivity, butadiene is estimated to have an atmospheric lifetime on the order of four hours, where atmospheric lifetime is defined as the time required for the concentration to decay to 1/e (37 percent) of its original value.[9] Actual lifetime depends on the conditions at the time of release. The primary removal mechanisms are through chemical reactions with hydroxyl radicals and ozone.[9] Therefore, factors influencing butadiene's atmospheric lifetime--time of day, sunlight intensity, temperature, etc.--also include those affecting the availability of hydroxyl radicals and ozone.

3.2 OVERVIEW OF PRODUCTION AND USE

Butadiene production in the United States is accomplished through either of two processes: recovery of butadiene from a mixed-C_4 hydrocarbon stream generated during ethylene production, or through oxidative dehydrogenation of n-butenes. Almost all, [1.47 millions tons (1.33 million megagrams) in 1993] results from recovery of butadiene as a byproduct of ethylene generation. Of the 10 U.S. producers, 8 are located in Texas and 2 in Louisiana.[8] The majority of these producers generate the feedstock at the same location as butadiene production.[8]

Seventy-five percent of butadiene is used in synthetic elastomer production, 30 percent of which is dedicated to styrene-butadiene rubber; 20 percent to polybutadiene; 10 percent to styrene-butadiene latex; and 5 percent each to neoprene, acrylonitrile-butadiene-styrene resin, and nitrile rubber. A second major use of butadiene is in adiponitrile production (15 percent), the raw material for nylon 6,6 production. The remaining 10 percent is used for miscellaneous products;[8] exports comprise less than 1 percent.[10] Figure 3-1 illustrates these uses and the subsequent consumer end products.[8,11,12,13,14,15,16]

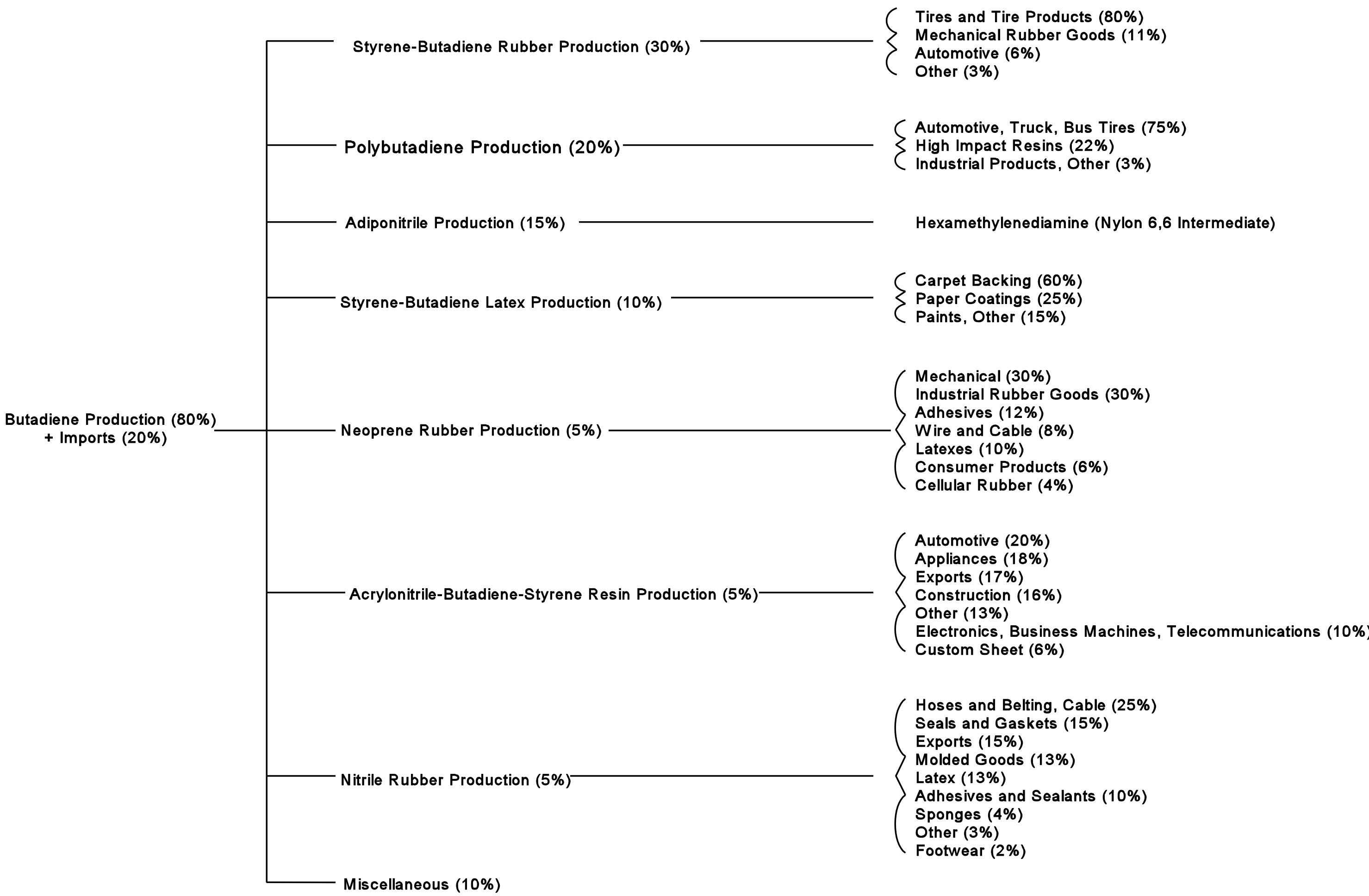

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Figure 3-1. Chemical Production and Use Tree for 1,3-Butadiene

Source: Reference 7, 10, 11, 12, 13, 14, 15

Long-term growth in demand for butadiene is expected to be modest, with reduced requirements for synthetic rubber because of quality and performance improvements in automobile and other road tires. There will be some newer butadiene applications (sealants, adhesives, processing aids for plastic industry) that will experience rapid growth in future years. However, overall U.S. butadiene demand growth is not expected to exceed 2 percent per year, and may well show a long term slow decline by 1995/1996.[10]

3.3 OVERVIEW OF EMISSIONS

Sources of butadiene emissions from its production and uses are typical of those found at any chemical production facility:

- process vents,
- equipment leaks,
- waste streams (secondary sources),
- storage, and
- accidental or emergency releases.

Much of the available emissions data used to prepare this report were collected by EPA from industry in 1984. Use of these estimates to represent sources at different locations is of limited accuracy because of the differences in process configurations and plant operations. The equipment leak emission factors are based on a 1989 CMA study. The CMA Butadiene Panel collected monitoring data from nine of the facilities manufacturing butadiene to develop average component-specific emission factors. Although the accuracy of applying these emission factors to butadiene user facilities is undetermined, they are presented as an alternative to the SOCMI emission factors previously developed by EPA.

Emissions data from several butadiene sources, including mobile, petroleum refining, secondary lead smelting, tire burning, and biomass burning, have been added to this update of the document and are described in Section 7.0.

Estimated national emissions from on-road mobile sources amount to 56,786 tons (51,517 Mg) based on butadiene emission factors developed by the EPA Office of Mobile Sources[17] and 1992 Department of Transportation data[18] on vehicle miles travelled. For nonroad mobile sources, the EPA Nonroad Engine Vehicle Emission Study (NEVES) provides an average estimate of 41,883 tons (37,996 Mg). Three nonroad categories are not included in the NEVES--locomotives, aircraft, and rockets. Of these, only estimates for general aviation and air taxis have been developed. These account for 61 tons (55 Mg) and 46 tons (42 Mg), respectively. For the other mobile sources, activity data were not readily available.

Estimates of national butadiene emissions from mobile and stationary sources are shown in Figure 3-2, and Figure 3-3 shows a breakdown of stationary source emission estimates. The estimates from butadiene production, major butadiene users, petroleum refining, and miscellaneous "other" sources are based on SARA 313 Toxic Release Inventory data for 1992. As mentioned above, the mobile estimates are based on EPA studies and Department of Transportation data. The secondary lead smelting and biomass burning (forest fires and prescribed burning) emission estimates are based on available emission factors combined with activity data. Appendix B describes the basis for all of the national emission estimates.

Some butadiene sources discussed in this document did not have enough data to estimate national emissions and are, therefore, not included in Figures 3-2 and 3-3. For example, an emission factor for butadiene from open burning of tires was found in AP-42, but the only available activity data were for tire incineration, not open burning.

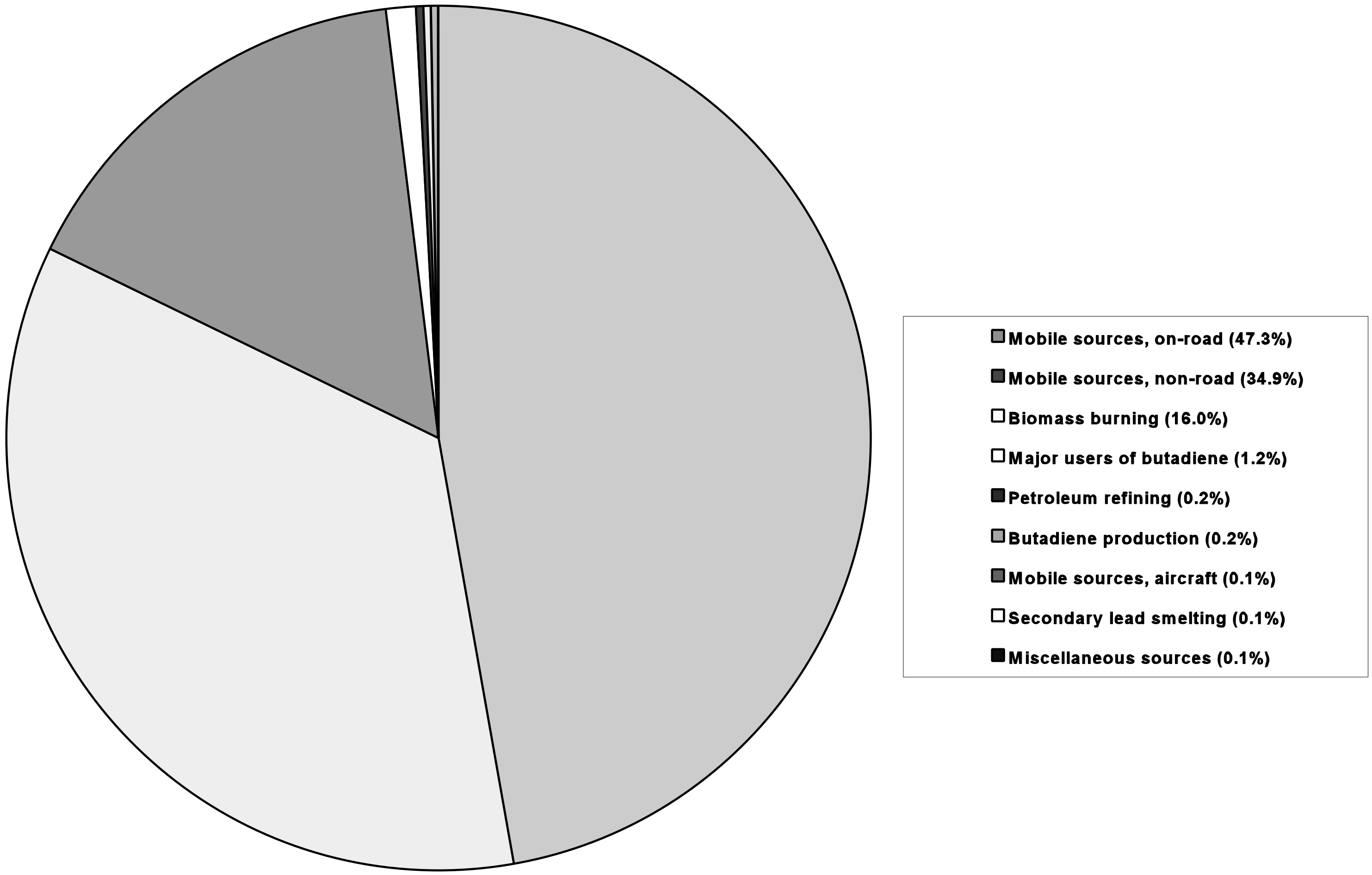


Figure 3-2. Relative Contributions to National Butadiene Emissions by Mobile and Point Source Categories

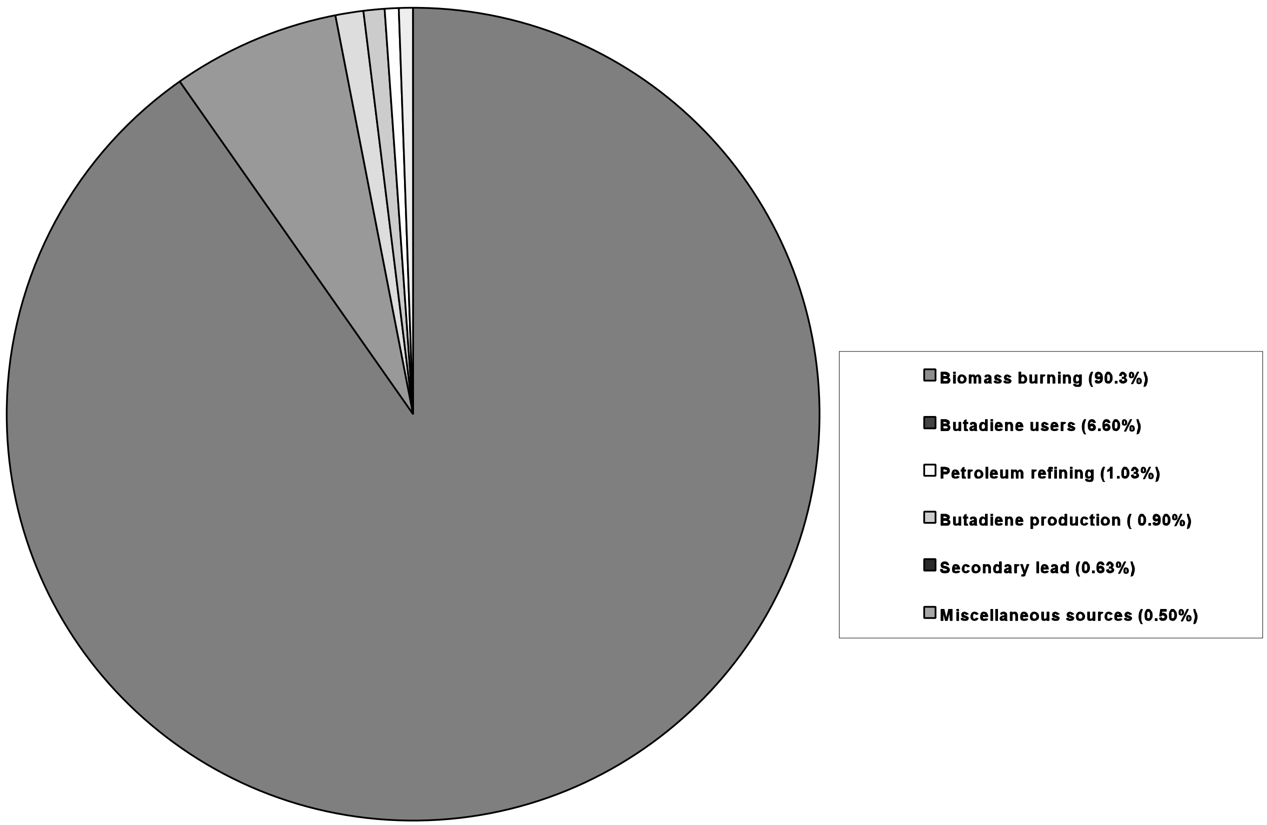


Figure 3-3. Relative Contributions to Stationary Butadiene Emissions by Point Source Categories

SECTION 4.0
EMISSIONS FROM BUTADIENE PRODUCTION

This section discusses emissions from sources associated with butadiene production. The information presented in this section includes identification of producers and descriptions of typical production processes. Process flow diagrams are given, as appropriate, with streams and vents labeled to correspond to the discussion in the text. Estimates of the associated butadiene emissions are provided in the form of emission factors when data were available to calculate them. Any known emission control practices are also discussed.

Much of the process vent and secondary source emissions data were taken from facility-reported information based on responses to Section 114 requests in 1984.[19] In many cases, these responses were incomplete. Interested readers should therefore contact specific facilities directly to determine the process in use, production volume, and control techniques in place before applying any of the emission factors presented in this document. This document will be reviewed for the need to provide newer data as they become available.

The equipment leak emission factors given in this section were calculated from producer screening data collected by the Chemical Manufacturers' Association (CMA) in 1988. This study is briefly described and the results presented both in terms of average component-specific emissions factors and as annual emissions.

4.1 BUTADIENE PRODUCTION

The 1,3-isomer of butadiene, the only commercially significant isomer, is a high-volume intermediate organic chemical used to produce various types of rubber, resins, and plastics. Butadiene is produced by two different processes in the United States. One process involves the recovery of butadiene from a mixed-C_4 hydrocarbon stream generated during ethylene or other alkene production. The other process is the oxidative dehydrogenation of n-butenes to produce butadiene.

The 10 facilities currently producing finished butadiene in the United States are listed in Table 4-1.[10] All of these facilities recover butadiene from a mixed-C_4 stream. The mixed-C_4 streams feeding the recovery units are produced at olefins units co-located with the recovery units at these facilities, with the exception of one facility that receives its feedstock from an unidentified source. This facility also has the capacity to produce butadiene using the oxidative dehydrogenation of n-butenes process. However, this capacity is being utilized to dehydrogenate isobutane to isobutylene, for use in the manufacture of tert-butyl-methyl ether (MTBE).[10]

4.1.1 Process Descriptions

Recovery of Butadiene from a Mixed-C_4 Stream

This process comprises two distinct steps. First, a mixed-C_4 stream containing butadiene is co-produced in an olefins plant during the cracking of large-molecule hydrocarbons to manufacture ethylene or other alkenes. The mixed-C_4 stream is then routed to a recovery unit, where the butadiene is separated.

The amount of butadiene produced during ethylene manufacture is dependent on both the type of hydrocarbon feedstock and the severity of the cracking operation. Typical butadiene yields from ethylene production, based on various feedstocks, are summarized in

TABLE 4-1. BUTADIENE PRODUCTION FACILITIES[a]

Company	Location	Capacity in 1993 tons/yr (Mg/yr)
Amoco Chemicals Company	Chocolate Bayou, TX	91,100 (82,000)
Occidental Petrochemical	Chocolate Bayou, TX	67,800 (61,000)
	Corpus Christi, TX	111,100 (100,000)
Exxon Chemicals Company	Baton Rouge, LA	156,700 (141,000)
	Baytown, TX	121,100 (109,000)
Lyondell Petrochemical Company	Channelview, TX	310,000 (279,000)
Shell Chemical Company	Deer Park, TX	126,700 (114,000)
	Norco, LA	252,200 (227,000)
Texaco Chemical Company	Port Neches, TX	317,800 (295,000)
Texas Petrochemicals Corporation[b]	Houston, TX	403,300 (363,000)

Source: Reference 10.

[a] The production process for all facilities is the recovery process. "Recovery" means butadiene as a coproduct in ethylene production is recovered from the mixed-C_4 stream.
[b] This facility is the only producer with on-purpose butylene dehydrogenation capacity, but this capacity is being utilized to dehydrogenate isobutane to isobutylene, for use in the manufacture of MTBE. This capacity is not included in the above totals. Effective January 1994, all of the Texas Petrochemicals operations will be owned by Huntsman Chemical.

Table 4-2.[19] Heavier feedstocks (naphthas and gas oils) produce much larger quantities of butadiene than do the lighter feedstocks.

A generalized block flow diagram of an olefins unit producing a mixed-C_4 co-product stream, excluding the ethylene separation process, is shown in Figure 4-1.[19] In olefins production, a steam cracking furnace is used to crack the hydrocarbon feedstock (Step 1). The heavy hydrocarbons are broken into two or more fragments, forming a stream of mixed hydrocarbons. The concentration of butadiene in this mixed hydrocarbon stream varies with the type of feedstock. The flue gas from the cracking furnace is vented to the atmosphere (Vent A).

TABLE 4-2. BUTADIENE YIELDS FROM RECOVERY USING A MIXED-C_4 STREAM PRODUCED FROM VARIOUS FEEDSTOCKS[a]

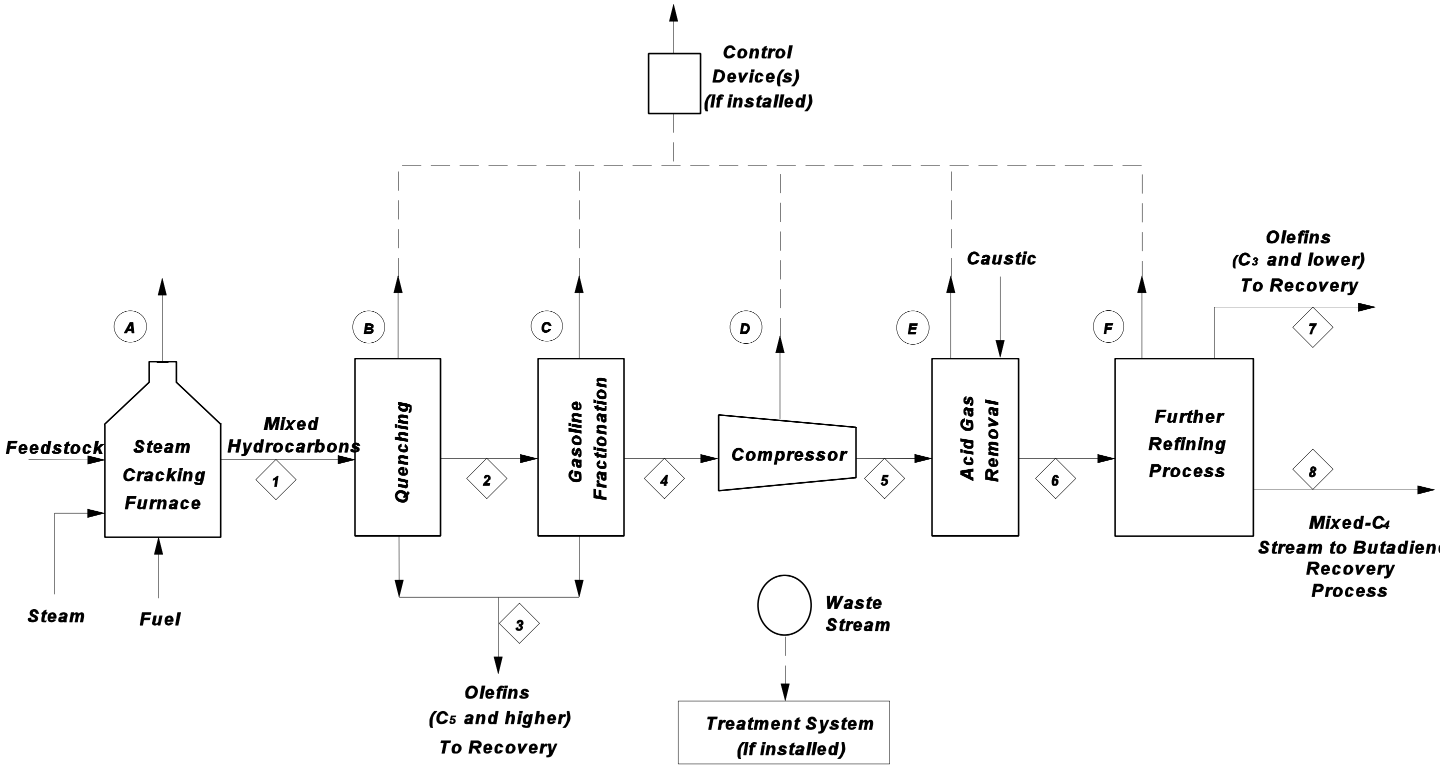
Feedstock	Yield Ratio (butadiene/ethylene produced on a weight basis)
Ethane	0.01 - 0.02
Refinery offgas	0.05
Propane	0.05 - 0.085
n-Butane	0.07 - 0.085
Naphthas	0.13 - 0.18
Gas oils	0.176 - 0.247

Source: Reference 19.

[a] Refer to Figure 4-1 for a process diagram of mixed-C_4 production olefins unit. Refer to Figure 4-2 for a diagram of a butadiene recovery process.

After the cracking step, the mixed hydrocarbon stream is cooled (Step 2) and, if naphtha or gas oils were the initial feedstock, the stream is sent to a gasoline fractionator (Step 3). The fractionator is used to recover heavy hydrocarbons (C_5 and higher). For some olefins units, the quenching step shown occurs after gasoline fractionation. The mixed stream is then compressed (Step 4) prior to removal of acid gas (hydrogen sulfide) (Step 5) and carbon monoxide. Acid removal usually involves a caustic wash step. The mixed hydrocarbon stream then goes through additional refining steps (Step 6), where it is separated from olefins (C_3 and lower).

The composition of a typical C_4 co-product stream from an ethylene plant using naphtha feedstocks is shown in Table 4-3.[20] The mixed-C_4 stream may be sent directly to butadiene recovery at the same plant. Olefins plants that do not produce finished butadiene may (1) recover the crude butadiene from the byproduct mixed-C_4 streams and sell it to a butadiene producer, (2) recirculate the stream into the front of the ethylene process, and/or (3) use the stream to fuel the equipment (e.g., furnaces) in the ethylene process.



Source: Reference 19

Figure 4-1. Process Diagram for Production of a Mixed-C_4 Stream Containing Butadiene

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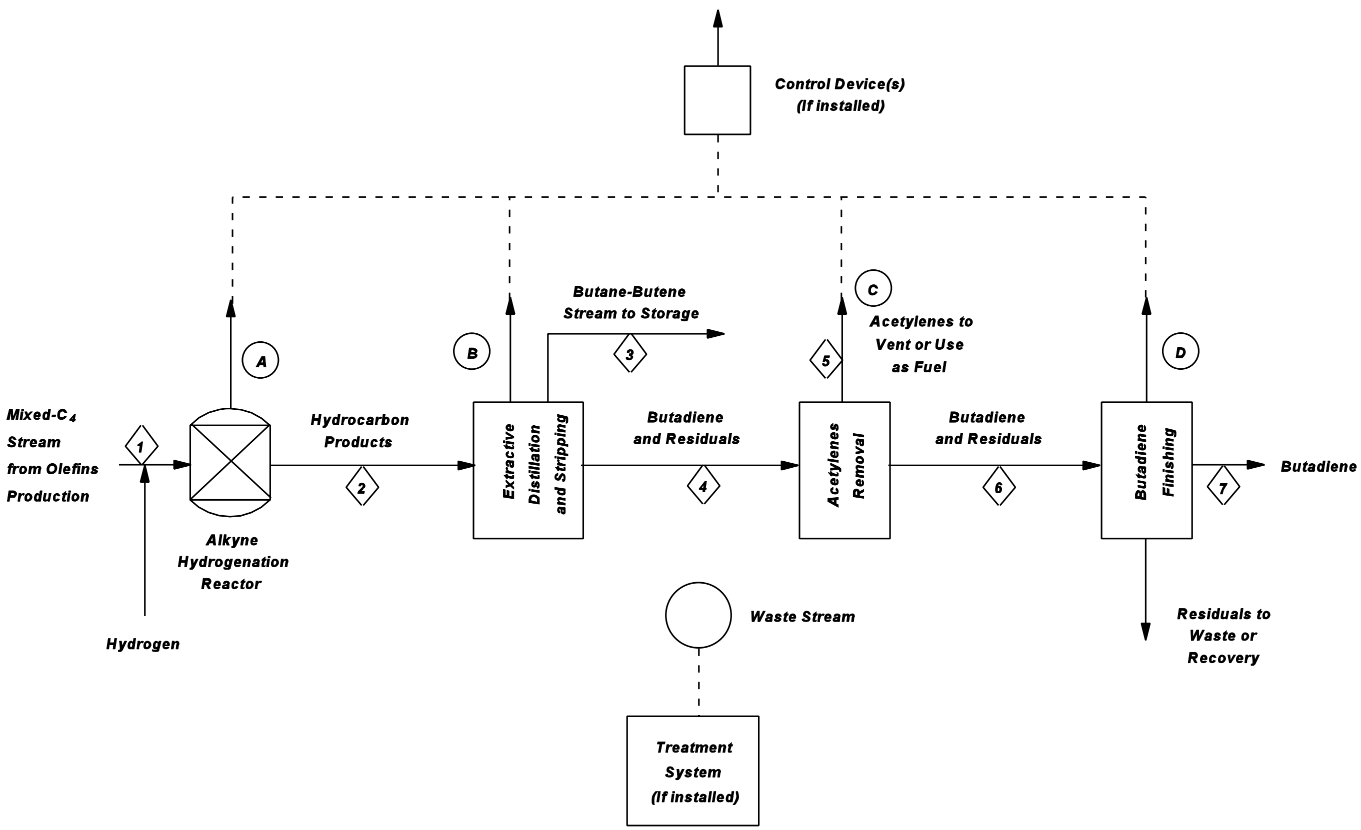
TABLE 4-3. TYPICAL COMPOSITION OF MIXED-C_4 STREAM FORMED FROM NAPHTHA FEEDSTOCK USED TO PRODUCE ETHYLENE[a]

Component	Molecular Formula	Composition (wt. %)
n-Butane	C_4H_{10}	6.80
Isobutane	C_4H_{10}	1.60
Isobutene	C_4H_8	29.00
1-Butene	C_4H_8	9.60
trans-2-Butene	C_4H_8	7.50
cis-2-Butene	C_4H_8	4.70
1,3-Butadiene	C_4H_6	39.30
1,2-Butadiene	C_4H_6	0.08
Propadiene	C_4H_4	0.53
Methyl acetylene	C_4H_4	0.65
Ethyl acetylene	C_4H_6	0.05
Dimethyl acetylene	C_4H_6	0.08
Vinyl acetylene	C_4H_4	0.11
TOTAL		100.0

Source: Reference 20.

[a] Refer to Figure 4-1 for process diagram of mixed-C_4 production.

The second part of this butadiene production process involves recovering the butadiene from the mixed-C_4 stream. A generalized block flow diagram of a butadiene recovery unit is shown in Figure 4-2.[19] The mixed-C_4 stream is fed from pressurized storage tanks into a hydrogen reactor along with hydrogen (Step 1) to convert some of the unsaturated hydrocarbons such as acetylene to olefins. The product C_4 stream from the hydrogenator is combined with a solvent (typically furfural) and fed into an extractive distillation operation (Step 2). In this operation, most of the butanes and butenes are separated from butadiene, which is absorbed in the solvent along with residual impurities. A stripping operation is then used to separate the butadiene from the solvent.



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Source: Reference 19

Figure 4-2. Process Diagram for Butadiene Production by Recovery from a Mixed-C_4 Stream

The stream containing butadiene typically has a small amount of residuals. Some of these residuals are alkynes that were not converted to olefins in the hydrogenation reactor. These residuals are removed from the butadiene stream by distillation (Step 3) and are usually vented to an emissions control device (Vent A). The bottom stream exiting the acetylenes removal operation contains butadiene and residuals such as polymer and 2-butene. The residuals are removed in the butadiene finishing operation (Step 4) and sent to a waste treatment system or recovery unit. The finished butadiene is then stored in pressurized tanks.

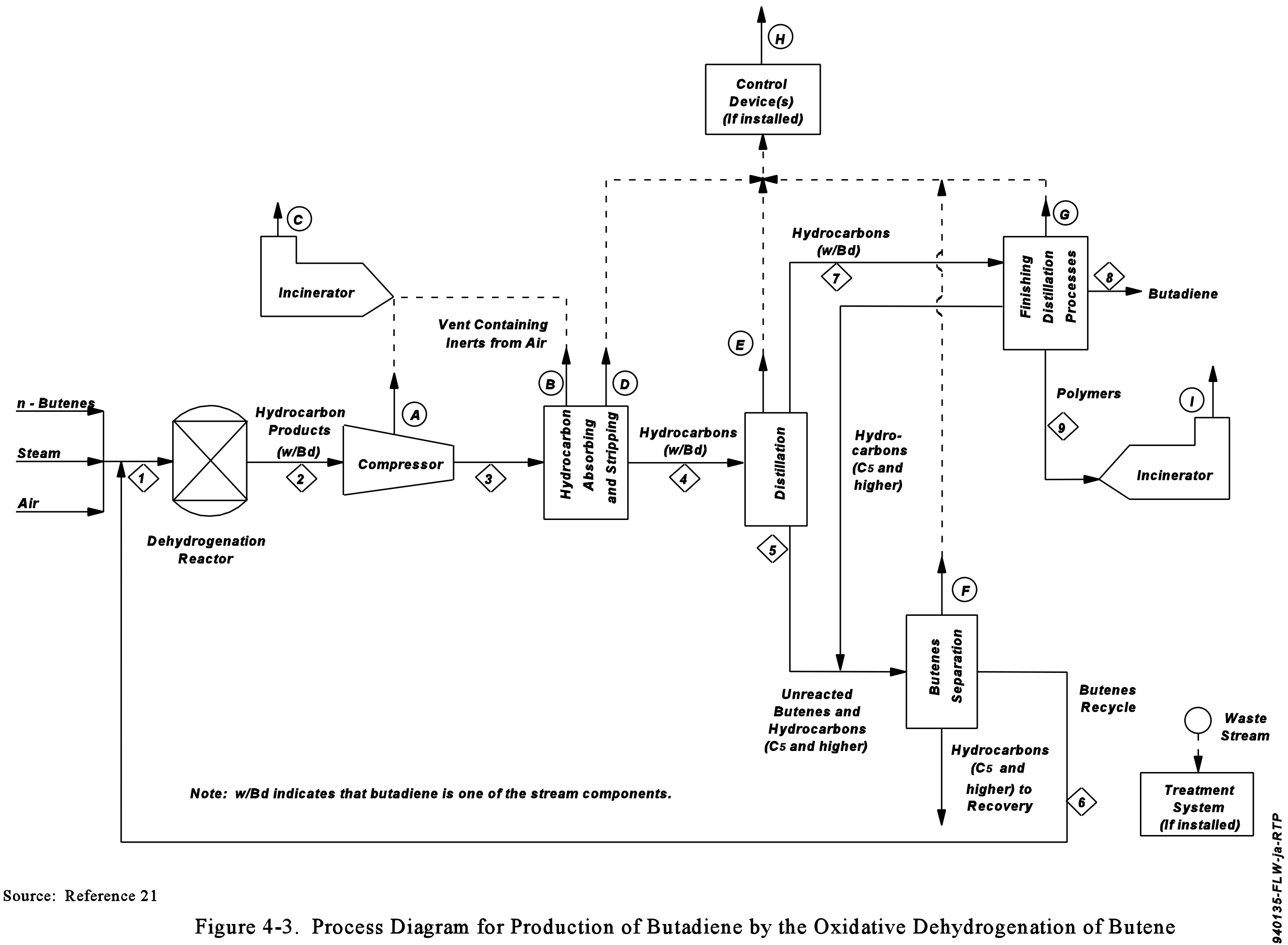
Oxidative Dehydrogenation of n-Butenes

The oxidative dehydrogenation of n-butenes (1- and 2-butenes) proceeds through the following primary reaction:

$$\left.\begin{array}{c} CH_2 = CH - CH_2 - CH_3 \\ \text{(1-butene)} \\ \text{or} \\ CH_3 - CH = CH - CH_3 \\ \text{(2-butene)} \end{array}\right. + \ 1/2\ O_2 \longrightarrow \begin{array}{c} CH_2 = CH - CH = CH_2 + H_2O \\ \text{(1,3-butadiene)} \end{array}$$

Between 2.4 and 2.9 pounds (1.1 and 1.3 kilograms) of n-butenes are consumed per pound (kilogram) of butadiene formed.

A generalized block flow diagram of the butenes dehydrogenation process is shown in Figure 4-3.[21] A feed stream of n-butenes is combined with steam and air, preheated, and passed through a dehydrogenation reactor (Step 1). Air is used as a source of oxygen to remove hydrogen from the butenes feed. The typical composition of a product stream is shown in Table 4-4.[21] The product stream is compressed after exiting the reactor (Step 2) and sent to a hydrocarbon absorption and stripping process (Step 3). During compression and absorption, vent streams containing nitrogen, excess oxygen, and volatile organic compounds (VOCs) are



Source: Reference 21

Figure 4-3. Process Diagram for Production of Butadiene by the Oxidative Dehydrogenation of Butene

TABLE 4-4. TYPICAL COMPOSITION OF n-BUTENES OXIDATIVE DEHYDROGENATION REACTOR PRODUCT STREAM[a]

Component	Molecular Formula	Composition (wt. %)
Oxygen	O_2	1.0
Nitrogen	N_2	15.8
Carbon oxides	CO, CO_2	3.0
Water	H_2O	65.0
Methane	CH_4	0.1
C_2's		0.3
C_3's		0.4
n-Butane	C_4H_{10}	0.4
Isobutane	C_4H_{10}	0.6
Isobutene	C_4H_8	1.1
1-Butene	C_4H_8	1.9
trans-2-Butene	C_4H_8	1.7
cis-2-Butene	C_4H_8	1.4
1,3-Butadiene	C_4H_6	7.2
C_5's		0.1
1,2-Butadiene	C_4H_6	Trace
Propadiene	C_4H_4	Trace
Methyl acetylene	C_4H_4	Trace
Ethyl acetylene	C_4H_4	Trace
Dimethyl acetylene	C_4H_6	Trace
Vinyl acetylene	C_4H_4	Trace

Source: Reference 21.

[a] Refer to Figure 4-3 for a process diagram of butadiene production by n-butenes oxidative dehydrogenation.

routed to an incinerator. The overhead stream from the hydrocarbon stripping column (not shown in Figure 4-3) is routed to a light-ends column for further separation.

The C_4 and heavier compounds (labeled hydrocarbons) exiting the absorption/stripping process are fed to a distillation operation (Step 4), where butadiene is separated from the unreacted n-butenes. The n-butenes stream exiting the distillation operation also contains C_5 and heavier hydrocarbons. This stream is routed to a separation process (Step 5), where n-butenes are recovered and recycled to the dehydrogenation reactor.

The stream containing butadiene from the distillation process (Step 4) is routed to a finishing distillation process (Step 7). At this point, finished butadiene is separated from other hydrocarbons and sent to pressurized storage. A polymer waste stream generated during the finishing process is routed to an incinerator. The hydrocarbons are sent to butene separation process units.

4.1.2 Emissions

Regardless of the process used to produce butadiene, emissions of butadiene at a production facility may be of five general types: process vent discharges, equipment leaks, emissions from secondary sources (wastewater, liquid waste, or solid waste discharges), storage-related releases, and emergency or accidental releases. In Figure 4-1, A through F are process vents, G represents an emission point after a control device. In Figure 4-2, the process vents are lettered A through D with E representing an emission point after a control device. In Figure 4-3, A through F are process vents, G, H, and I are emission points after control devices.

No information about emissions associated with storage or emergency/ accidental releases is available. Storage vessel discharges may be assumed to be negligible because butadiene is stored in pressure vessels that have no breathing or working losses. Some losses during transfer of butadiene are possible if the butadiene is not used on site. However, these losses should be low because the butadiene has to be transferred under pressure without release points.

Emissions are presented in the form of emission factor ranges for process vents and secondary sources. Individual emission factors having units of pounds (kilograms) of butadiene emitted per ton (megagram) of butadiene produced were first calculated for each facility by dividing facility-specific estimates by production, taken as 80 percent of capacity.[19] From these facility-specific emission factors, a range for each source was established. The values of "n" indicate the number of facilities included. Because facilities reported varying levels of controls, two sets of emission factor ranges were developed. One range reflects actual facility emissions in which each facility may control all, some, or none of its sources. The second range incorporates both emissions from existing uncontrolled sources and potential emissions from controlled sources if controls had not been in place.

Equipment leak emissions are based on equipment count data collected by CMA in 1989 and average CMA emission factors for butadiene producers.

Facility-specific emissions estimates and capacity data appear in Appendix C, Tables C-1 through C-4. These emission factor ranges and annual emissions should be used only as order-of-magnitude approximations because differences in production processes and control levels, among other variables, may significantly influence actual emissions.

Process Vent Discharges

Process vent discharges occur from reactor vessels, recovery columns, and other process vessels. They may occur continuously (from a continuous process) or intermittently (from a batch process). Some continuous processes also have intermittent VOC emissions during startup and shutdown, or during control device malfunction or process upsets.

The possible locations of these process vents are shown in Figures 4-1 through 4-3. The actual locations and butadiene content may vary depending on the particular facility design. In many cases, process vents are directed to other parts of the plant or to a gas recovery system for use as fuel rather than discharged to the atmosphere.

Emissions data, including the use of control devices (six facilities use flares, of which two also have fuel gas recovery systems), were available for some facilities (see Appendix C). An emission factor range derived from these data is presented in Table 4-5. Also included in the table is an uncontrolled emission factor range to provide an indication of the extent to which controls are used. These were calculated from controlled emission factors using the emissions reduction efficiencies listed in Table 4-6.[22,23,24] It should be noted that use of these factors introduces uncertainty. Many flares and incinerators achieve greater than 98 percent control. If 99 percent were used as a factor instead of 98, uncontrolled emissions estimates would double.

Processes for both olefins production and butadiene production via oxidative dehydrogenation are potential sources of emissions. However, the emissions data are limited to the olefins process at the two facilities. One of the facilities is reportedly controlling process vents on the oxidative dehydrogenation process at the hydrocarbon absorbing and stripping column and at the compressors (incinerator and flare) (see Figure 4-3).

Equipment Leak Emissions

Emissions from process equipment components occur when the liquid or gas process streams leak from the equipment. These components include pump seals, process valves, compressors, safety relief valves (pressure relief devices), flanges, open-ended lines, and sampling connections.

The emissions estimates shown in Table 4-5 are the results of a study conducted by CMA.[25] The study's objective was to develop industry-specific emission factors to replace SOCMI emission factors[26] because the SOCMI emission factors were thought to overestimate equipment leak emissions for butadiene producers. The study recommends, however, that screening data and correlation equations (also revised) be used to generate the most accurate estimates.

TABLE 4-5. SUMMARY OF EMISSION FACTORS FOR BUTADIENE PRODUCTION FACILITIES (FACTOR QUALITY RATING E)

Emission Sources	Facility Emission Factors[a,b,c] Range	Facility Emission Factors[a,b,c] Mean	Uncontrolled Emission Factors[a,b] Range	Uncontrolled Emission Factors[a,b] Mean
Process Vents:				
C_4 stream production 3-01-153	---	---	0.0054 lb/ton (0.0027 kg/Mg)	---
Recovery process 3-01-153-01	0.0068 - 0.0550 lb/ton (n=3) (0.0034 - 0.0275 kg/Mg)	0.0314 lb/ton (0.0157 kg/Mg)	0.0322 - 0.6872 lb/ton (n=3) (0.0161 - 0.3436 kg/Mg)	0.4652 lb/ton (0.2326 kg/Mg)
Secondary Sources:				
Recovery process - wastewater 3-01-153	0.00068 - 4.4 lb/ton (n=6) (0.00034 - 2.2 kg/Mg)	0.936 lb/ton (0.468 kg/Mg)	---	---
Recovery process - solid waste 3-01-153	Negligible[e] (n=2)	---	---	---

Source: References 19 and 25.

Note: Annual emissions from equipment leaks, recovery process (SCC 3-01-153-80), are 455 tons/yr (407 Mg/yr) (n=9)[a,c,d]

[a]Assumes production capacity of 80 percent.
[b]Factors are expressed as lb (kg) butadiene emitted per ton (Mg) produced.
[c]Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.
[d]Total number of components is 79,430: 60 percent flanges, 29 percent liquid valves, 8 percent gas valves, and 3 percent all others combined.
[e]Defined as 0.4988 x 10^{-6} kg/Mg.

"---" means no data available.
n = number of facilities.

TABLE 4-6. VOC EMISSIONS REDUCTION EFFICIENCIES OF CONTROL DEVICES USED TO ESTIMATE CURRENT BUTADIENE EMISSIONS

Control Device[a]	Reduction Efficiency (%)	Reference
Gas recovery (boiler)	99.9	21
Flare	98	22
Incinerator	98	23

[a] Devices reported by industry to control vent streams and secondary emissions. Possible placement of control devices are shown in Figures 4-1 through 4-3.

The Butadiene Panel of CMA designed its study to closely adhere to EPA protocols for generating unit-specific emissions estimates as specified in the 1987 draft *Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP*. In addition to using the protocols, the Butadiene Panel sought EPA comments on the procedure before it began collecting data. Nine of the 11 finished butadiene producers in the United States participated in the study. The exceptions were the Shell facility in Norco, Louisiana, which was not in service, and the Texas Petrochemical facility in Houston, Texas. Four facilities that produce only crude butadiene also contributed data: three Union Carbide plants in Seadrift, Texas, Taft, Louisiana, and Texas City, Texas; and Dow Chemical in Freeport, Texas. All of these facilities produce butadiene by the recovery process. No estimate of equipment leak emissions from the oxidative dehydrogenation process was possible because of the lack of equipment component counts.

Based on facility data, ranges of butadiene concentrations through equipment components were established. Weighted average percents were calculated from the number of each component in each range. Approximately 20 percent of components were associated with butadiene streams having between 5-30 percent concentration, 47 percent with the 30-90 percent butadiene range, and 33 percent with the 90-100 percent butadiene range.

The screening data collected were similarly grouped into ranges of concentration [parts per million (ppm)] based on the instrument readout and the butadiene concentration in the stream. Five ranges from 0-9 to >9999 ppm were used. Upon calculating weighted average percents, about 76 percent of components fell in the 0-9 ppm range and 19 percent in the 10-99 ppm range. Fewer than 6 percent were found to be greater than 100 ppm. Table 4-7 summarizes the study results.[25]

In addition to average emission rates, average butadiene concentration in the stream through each type of component is shown. These average concentrations were used to convert SOCMI emission factors from units of VOC emissions to butadiene emissions for purposes of comparison to the new emission rates. The results of this comparison are also given in Table 4-7.

In addition to compiling the data from all facilities, the study analyzed the data on a plant-specific level. Table 4-8 provides the variability among the plants by component type determined from this analysis.[25]

The emissions shown in Table 4-7 include the reduction achieved by the various controls in place at the 13 facilities. The Butadiene Panel conducted a survey to identify and evaluate practices in the plants that would contribute to emissions reductions. Of the six respondents, all stated that they monitor fugitive emissions using a combination of visual observation and automatic audible alarm for specific equipment such as pumps and compressors. Three plants have routine leak inspection and maintenance programs. Two plants informally require immediate repair of leaks detected by the monitoring system. Five of the six plants reported combinations of visual inspections, pressure testing, VOC monitoring, use of double-sealed pumps, seals vented to a flare, bubble-testing flanges, tightness testing of valves, use of special packing material, closed-loop sampling points, and plugging of all open-ended lines. No estimate of the emissions reductions achieved by these practices was determined.

TABLE 4-7. AVERAGE BUTADIENE EMISSION RATES FOR PROCESS EQUIPMENT COMPONENT LEAKS

Equipment Component (Emission Source)	Average Emission Rate[a] (lb/hr/component)	Average Butadiene Concentration (%)	Reduction[b] (%)
Pumps - Liquid	0.05634		
	(0.02555)	64.1	19.3
Compressors	0.000004		
	(0.0000018)	27.9	99.9+
Flanges	0.000307		
	(0.000139)	61.0	72.5
Valves - Gas	0.001105		
	(0.000501)	60.2	85.1
Valves - Liquid[c]	0.003140		
	(0.001424)	59.7	66.3
Pressure Relief Devices	0.02996		
"Safety Valves"	(0.013590)	56.7	76.9
Sampling Point[d]	-	-	-
Open-ended Lines	0.000120		
	(0.000054)	67.9	95.2

Source: Reference 25.

[a] The average emission rate has been derived from facility data, some of whom are using controls. Numbers in parentheses are in units of kg/hr/component.

[b] Calculated as $\left[1 - \frac{\text{CMA emission factor}}{\text{SOCMI emission factor}}\right] \times 100$

[c] Liquid refers to light liquid and is defined as a petroleum liquid with a vapor pressure greater than the vapor pressure of kerosene.

[d] Sampling points were considered to be a subset of open-ended lines; therefore, data were incorporated in the open-ended line average emission factor.

TABLE 4-8. VARIABILITY IN FACILITY-SPECIFIC EMISSION RATES FOR EQUIPMENT LEAKS

Equipment Component	Relative Standard Deviation (%)
Pumps - Liquid	96.0 (n=13)
Compressors	137.4 (n=3)
Flanges	91.4 (n=13)
Valves - gas	84.3 (n=13)
Valves - liquid	45.2 (n=13)
Pressure Relief Devices	226.6 (n=10)
Open-ended Lines	117.8 (n=6)
Sample points	102.1 (n=4)

Source: Reference 25.

In the absence of specific information relating controls in use to reduction achieved, previously developed control efficiencies are presented in Table 4-9 to provide an indication of typical reductions achieved. For leak detection and repair programs, EPA has provided a method for estimating the emission reductions in *Protocol for Equipment Leak Emission Estimates*.[1] The reader is referred to this document for this information. To apply these efficiencies and determine emissions after controls, an estimate of uncontrolled emissions would be multiplied by [1-(efficiency/100)]. More information on estimating uncontrolled emissions is provided in Appendix D.

TABLE 4-9. CONTROL TECHNIQUES AND EFFICIENCIES APPLICABLE TO EQUIPMENT LEAK EMISSIONS

Equipment Type	Modification	Approximate Control Efficiency (%)
Pumps	Sealless design	100[a]
	Closed-vent system	90[b]
	Dual mechanical seal with barrier fluid maintained at a higher pressure than the pumped fluid	100
Compressors	Closed-vent system	90[b]
	Dual mechanical seal with barrier fluid maintained at a higher pressure than the compressed gas	100
Pressure relief devices	Closed-vent system	[c]
	Rupture disk assembly	100
Valves	Sealless design	100[a]
Connectors	Weld together	100
Open-ended lines	Blind, cap, plug, or second valve	100
Sampling connections	Closed-loop sampling	100

Note: Based on Reference 1. Butadiene emissions were assumed to be reduced by the same percentage as VOC emissions.

[a] Sealless equipment can be a large source of emissions in the event of equipment failure.
[b] Actual efficiency of a closed-vent system depends on percentage of vapors collected and efficiency of control device to which the vapors are routed.
[c] Control efficiency of closed-vent systems installed on a pressure relief device may be lower than other closed-vent systems, because they must be designed to handle both potentially large and small volumes of vapor.

Secondary Emissions

Secondary emissions occur during the treatment and disposal of wastewater, other liquid waste, and solid waste. Few emissions estimates are available, and most of these data pertain to wastewater from the butadiene recovery process. Table 4-5 summarizes emission factors derived from the estimated wastewater and solid waste emissions in Appendix C. No factors are available for the olefins process, the oxidative dehydrogenation process, or for any liquid waste other than wastewater. The types of waste streams generating butadiene emissions include cooling water, wash water, solvent recovery wastewater, process unit wastewater, and waste polymer.

Because of its volatility and low solubility in water, butadiene in a waste stream is assumed to completely volatilize unless the vapor is routed to a control device. Some facilities use such emission control systems; others do not. Available information on facility control status and handling of the waste streams in 1984 is summarized in Appendix C.